Unusual Pyramidal Folding of Methylene Groups in a Trimethylene Diradical Structure

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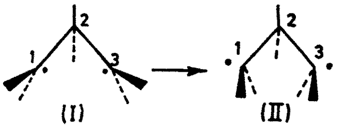
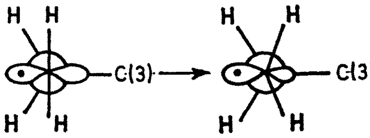
Summary A "crab-like" structure (II) is described for the face-to-face trimethylene diradical, characterized by pyramidal collapse of the terminal methylene groups towards the inside of the open ring; the stabilization (6·2 kcal mol^{-1}) of the singlet state is accounted for by mixing of strong zwitterionic character into the diradical wave function.

IN our studies, by *ab initio* SCF methods, of the reaction paths for the geometrical isomerization of cyclopropane,[1] we found an unusual pyramidal configuration of a terminal methylene group in the orthogonal face-to-edge trimethylene diradical.[2] We now report a structure, the face-to-face trimethylene diradical obtained by the stretching of one C–C bond in cyclopropane, in which the pyramidal folding of both terminal methylene groups occur in an unexpected way. The expected "open" cyclopropane with trigonal terminal methylene groups (I) collapses into a "crab-like" structure (II) in which both terminal CH_2 groups are strongly folded inwards.

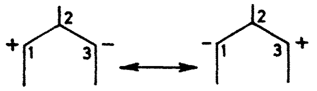


(I) (II)

The stabilization energy is $-6{\cdot}2$ kcal mol^{-1} in the singlet state but only $-0{\cdot}9$ kcal mol^{-1} in the triplet state (the central C–C–C angle is 113°). This difference indicates that two effects are involved: a minor effect, to which both singlet and triplet are sensitive and a major effect, to which only the singlet state is sensitive. The minor effect is probably of a conformational nature and may be ascribed to the increased staggering of the terminal methylene groups relative to the central CH_2 group.‡ This local steric relief was *ca.* 1 kcal mol^{-1} for one methylene group in the face-to-edge diradical.[1a]



The additional stabilization of the singlet state must be due to an electron-pairing effect. The wave functions of (I) and (II) show that the singlet state has recovered some closed-shell character and that bonding between C-1 and C-3 has been restored. However, the overlap between the odd atomic orbitals on C-1 and C-3 decreases as the inner lobes get smaller and the outer lobes greater. The only alternative is that the system must be acquiring ionic character. Indeed the stability of (II) can be interpreted classically, in terms of resonance between two zwitterionic structures, equation (1). This resonance and concomitant energy stabilization more than outweighs the loss due to the lesser orbital overlap. The negative region of the zwitterion is of course stabilized by the pyramidalization, since C^- is isoelectronic with N. The positive region should be relatively insensitive to pyramidalization; although the methyl cation is certainly planar, calculation on the ethyl cation[3] and on the propyl cation[4] show stable geometries in which the CH_2^+ group is distorted slightly from a trigonal towards tetrahedral configuration. Furthermore the stabilization of the positive charge by hyperconjugation from the central CH_2 group should be made easier by direct electron transfer from this group to the large lobe on C-1 (or C-3) along the outer edge of the C(2)–C(1) [or C(2)–C(3)] bond.§ This would not be the case if the pyramidalization had occurred outwards, with the large lobes pointing towards the inside of the ring.



(1)

The singlet state energy of (III), in which only a single methylene group has pyramidalized, is slightly (0·6 kcal mol^{-1}) higher than the midpoint in the passage from (I) to (II) *via* synchronous folding of the terminal group. The right hand resonance structure is particularly stable in this conformation, but the left hand resonance structure should have a prohibitively large energy. Overall, the energy gain is not quite as good as in the symmetric folding process. We have verified that in (III), C-3 is negatively charged, while C-1 is positively charged. The net charge on each atom is *ca.* 0·1 atomic units.

We conclude that in the face-to-face trimethylene system ionic bonding is created at the expense of covalent bonding. The molecule deliberately sacrifices overlap to improve its "ion-pair" character, in what might be called a "sacrificial"

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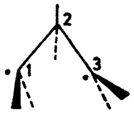
‡ In a recent calculation on the ethyl radical, W. A. Lathan, W. J. Hehre, and J. A. Pople (*J. Amer. Chem. Soc.*, in the press) found a methylene pyramidalization similar to that of the face groups in (II). The local out-of-plane angle of the CH_2 group is 22·9°, compared with 32° for the methylene groups here (*i.e.* roughly half-way between pure trigonal and pure tetrahedral hybridization). The same SCF calculation yields only a very weak pyramidalization of the methyl radical (HCH angle, 118·3° out of plane angle, 7·6°; barrier to inversion, 0·2 kcal mol^{-1}). See also Table I of S. Y. Chang, E. R. Davidson and G. Vincow, *J. Chem. Phys.*, 1970, **52**, 5596. In this respect one should be wary of assigning too much significance to energy differences smaller than 1 kcal mol^{-1}, which may be due to the minimal nature of the basis set and the restricted nature of the SCF wave function.

§ We have verified that the coefficients of the CH_2 group orbitals in the top bonding molecular orbital (containing the "broken" electron pair) are of *opposite* sign to those of the outer lobes on C(1) and C(3), as required for such a hyperconjugative effect (see ref. 5).

type of bonding. We also observed less important pyramidal folding, of purely conformational origin, of edge-terminal methylene groups in the face-to-edge orthogonal diradical and in the edge-to-edge "coplanar" diradical. The details will be given elsewhere.[1c]

The mechanistic consequences of (II) may be serious. The collapse of open cyclopropane into structure (II), which is more stable than either the face-to-edge diradical [1a,b] or the edge-to-edge diradical[5,1b] by at least 2 kcal mol^{-1} in the singlet manifold, raises the question as to whether (II) corresponds to the kinetically observed metastable trimethylene intermediate.[6] However, preliminary calculations show no "barrier to reclosure"[6] from (II) to cyclopropane. Thus outwards inversion of the terminal methylene groups towards their original conformation in cyclopropane and concurrent C(1)–C(3) bond closure can apparently occur simultaneously without any energy loss.¶ Furthermore the zwitterionic character of (II) may also have serious implications concerning both the degree of stereospecific behaviour of trimethylene and the extent of concertedness of the CH_2 internal rotations.[7] We are presently studying these consequences.



(III)

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¶ P. von R. Schleyer (personal communication, 1970) pointed out that the overall process which leads from cyclopropane to (II) can be thought of as one where C-1 and C-3 move apart while the terminal hydrogens stay fixed in the same position as in cyclopropane itself. The reverse motion will not require any movement of the hydrogens either.

[1] (a) L. Salem, *Bull. Soc. Chim. France*, 1970, 3161; (b) L. Salem, 21st Congress (Sept. 1970) of the Société de Chimie Physique on the Transition State, Gordon and Breach, Publishers, in the press; (c) L. Salem, R. Stevens, J. Horsley, Y. Jean, C. Moser, and J. S. Wright, to be published.

[2] We use the terminology "face-to-face," "face-to-edge," and "edge-to-edge" (E. W. Yankee and D.J. Cram, *J. Amer. Chem. Soc.*, 1970, **92**, 6331) to describe the three different limiting diradical entities in trimethylene.

[3] (a) J. E. Williams, jun., V. Buss, L. C. Allen, P. von R. Schleyer, W. A. Latham, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, 1970, **92**, 2141; (b) W. A. Latham, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, in the press.

[4] L. Radom, J. A. Pople, V. Buss, and P. von R. Schleyer, *J. Amer. Chem. Soc.*, in the press.

[5] R. Hoffmann, *J. Amer. Chem. Soc.*, 1968, **90**, 1475.

[6] B. S. Rabinovitch, A. W. Schlag, and K. B. Wiberg, *J. Chem. Phys.*, 1958, **28**, 504; S. W. Benson, *ibid.*, 1961, **34**, 521.

[7] E. W. Yankee and D. J. Cram, *J. Amer. Chem. Soc.*, 1970, **92**, 6328, 6329, 6331, have studied various highly substituted trimethylene intermediates whose chemical behaviour is consistent with simultaneous zwitterionic and covalent character.